

Properties of Home Made Spin Coated TiO₂ Thin Film

T. ARIVUDAINAMBI, S. SAKTHIVEL* and C. MANICKARAJAN

PG and Research Department of Physics, Rajah Serfoji Govt. College,
Thanjavur-613005, Tamilnadu, India

ABSTRACT

Titanium dioxide Thin film were formed over well cleaned glass substrate. by home made spin coating technique. For structural analysis XRD spectrum were taken at 300 and annealed temperature 400° C. The thicknesses of the titanium dioxide thin film were measured by using gravimetric technique. FTIR spectrum confirmed the position of titanium and oxygen TiO₂ thin film. UV and Absorbance spectrum used for calculating the band gap energy E_g of the titanium dioxide thin film. SEM photograph of the annealed TiO₂ thin film were taken for surface analysis.

Keywords : Thin film, TiO₂ , spin coating , XRD, Band gap, Transmittance, Absorbance

INTRODUCTION

Now a days thin film of metals, semiconductors and dielectrics have been gaining increasing importance for fundamental studies in many fields of physics, electronics and chemistry and are also employed in numerous practical applications. Electronic semiconducting` devices are mostly depend the thin film technology. A thin film is the two dimensional material born of an atom-by-atom or molecule-by-molecule condensation process.

Thin film science now covers a wide span of a discipline such as solid state physics, nano physics, surface science, crystallography, crystal growth process, optics, electronics, material science etc., the distinction between thin film and thick film

technology is that the former involves deposition of individual molecules, while the latter involves deposition of particles. For example painting, silk screening, spin on glass coating, and plasma spraying. This technique is inexpensive, but, they don't offer the material quality of thin film. Temperature is a key parameter playing in changing film properties.

As a pigment of high refringence, titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index ($n=2.4$), which is surpassed only by a few other materials. When deposited as a thin film, its refractive index and colour make it an excellent reflective optical coating for dielectric mirrors and some gemstones, for example "mystic fire topaz". TiO₂ is also an effective opacifier in powder form, where it

is employed as a pigment to provide whiteness and opacity such as paints, coating, plastics, papers, inks, foods, and most toothpastes. In cosmetic and skin care products, titanium dioxide is used both as a pigment and a thickener. It is also used as a tattoo pigment and styptic pencils. In ceramic glazes titanium dioxide acts as an opacifier and seeds crystal formation. In almost every sunscreen with a physical blocker, titanium dioxide found both because of its refractive index and its resistance to discoloration under ultraviolet light. This advantage enhances its stability and ability to protect the skin from ultraviolet light. Sunscreens designed for infants or people with sensitive skin are often based on titanium dioxide and/or zinc oxide, as these mineral UV blockers are less likely to cause skin irritation than chemical UV absorber ingredients.. Titanium oxide is also used as a semi-conductor thin film. The nano structure of TiO_2 , stability can be make as a suitable gas sensor, for the purpose of exhaust gases the sensing layer proved capable to detect 20 ppm (1-4) and for electrochromic devices (5).

EXPERIMENT

Spin coating technique is used to apply uniform thin films on flat substrates. In short, an excess amount of the solvent is placed on the substrate. Which is then rotated at high speed in order to spread the fluid by centrifugal force. A machine used for spin coating is called a spin coater or simply spinner.

Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher

the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. Spin coating is widely used in micro fabrication, where it can be used to create thin films with thicknesses below 10 nm. The temperature and atmosphere in the chamber environment can be precisely controlled to ensure high quality results .

A typical process involves depositing a small puddle of liquid resin onto the centre of a substrate and then spinning the substrate at a very high speed. Centripetal acceleration will cause most of resin to spread to, and eventually off, the edge of the substrate, leaving a thin film resin on the surface. Final film thickness and other properties will depend on the nature of the resin and the parameters used for the spin process. One of the most important factors in spin coating is repeatability. Suitable variations in the parameters that define the spin process can result in drastic variation in coating film. . A speed of about 500 rpm is commonly used during this step of the process. This servers to spread the fluid over the substrate and can result in less waste of resin material since it is not usually necessary to deposit as much to wet entire surface of the substrate itself has poor wetting ability and can eliminate voids.

Number of factors affecting the coating process, they are spin speed, acceleration, spin time and exhaust, process parameters vary greatly for different resin materials and substrate so there are no fixed rules for coat processing.

Titanium dioxide thin films were prepared by the preparation of Titanium dioxide precursor solution. Titanium tetra isopropoxide (TTIP) has been used as a Ti

source material and ethanol was served as a solvent. We have used acetylacetone as a stabilizing agent. Solution of 1.2 ml TTIP was mixed with 10 ml of ethanol. The solution becomes milky white. Then 1 ml of acetylacetone was added with the solution. Suddenly, the solution becomes transparent yellow color, these processes were carried out with constant stirring, and after 30minute's again 10 ml ethanol was added for the complete hydrolysis and condensation. Then the solution was stirred for 3 hours continuously. Finally thus prepared solution has been used for thin film coating.

The thin film coating was made on to the glass substrates. The substrate was etched with HF and water solution in 1:9 ratios. After the etching it was cleaned with detergent and distilled water. Finally they were ultrasonically cleaned in Acetone. Then they were dried at 100° C for 1 hour in hot air oven.

The substrate was mounted on the home made spin coater. The coating solution was dropped over the glass substrate using dropper. Then the spinner has rotated at 2500 rpm for 20 seconds. Thus one layer of thin film was coated on the substrate. Then it was subjected to heat treatment at 150°C for 15 minutes for the removal of the organic material. After this, the second coating was made as mentioned previously. Thus five coatings were made for each film. Finally the spin coated thin films were annealed at 300°C, 400°C, 500°C for 2 hour in muffle furnace.

X-rays diffraction studies were carried out at 300 and annealed temperature 400° C. are generated both by the deceleration of electrons in metal targets and by the excitation of the core electrons having

a strong line (CuK α line) at 1.5418 Å. XRD analysis used to study in structure determination, chemical analysis stress measurement, study of phase equilibrium particle size, determination of orientation of a single crystals or orientations of polycrystalline aggregate.

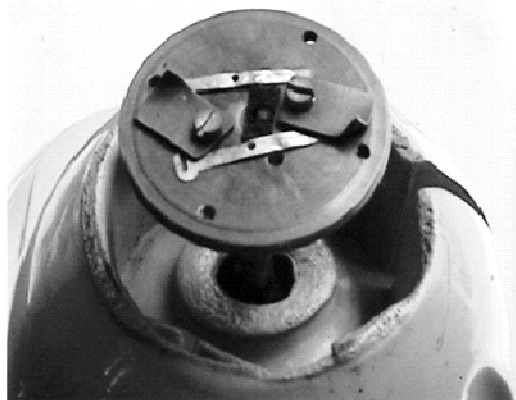


Fig. 1 Photograph of homemade spin coater

The source and the detector are the conventional ones that are used in IR spectrometer. A small computer is employed to control the scan system and carry out the mathematical transformation. The heart of the system is the mirror scan mechanism. For faithful reproduction of the spectrum from the interferogram, the detector output must be known as a function of mirror displacement. The measurement of mirror displacement becomes increasingly difficult as the wavelength decreases. At short wavelengths, a special technique is used. Here, one transducer is used to drive simultaneously the movable mirrors of two interferometers through identical displacements. Sample radiation passes through one interferometer and produces the sample interferogram. Reference interferogram is recorded using a He—Ne laser, the reference laser ensures that sampling of

the detector signal occurs reproducibly from scan to scan. Since the interferogram of a monochromatic source (laser) is a sine wave, its zero crossings, provide as accurate trigger for digitized data collection of the main interferogram. Further, use of He-Ne laser reference interferogram provides an integral frequency calibration important to high resolution studies.

Fourier transform infrared (FTIR) spectroscopy is rapidly becoming a common feature in modern spectroscopy laboratories. A wide range of commercial FTIR spectrometers with very different specifications are available now. This has become possible with the availability of inexpensive microcomputers. Fourier transform technique depends upon the basic principles that any wave function could be represented as a series of sine and cosine functions with different techniques. Using the Fourier Transform (FT) into practice can become tedious and time consuming even when using computers. This situation was considerably caused by the invention of past Fourier transformation algorithm by Cooley and Tukey in 1965, which made it possible to carry out FT of complex data in matter of few seconds. Most of the present day applications of FT analytical techniques are dependent on Cooley Tukey, FT.

UV-VIS-NIR spectrometer features a continuous change in wavelength and an automatic comparison of light intensities of sample and reference material the ratio of the latter is the transmittance of the sample which is plotted as a function of wavelength. The automatic operation eliminates many time consuming adjustments and provide rapid spectrogram. These instruments are well suited for qualitative analysis where complex curves must be obtained over a

large spectral range. In the double beam in time arrangements energy from a dispersed source passes through the exit slit of the monochromator and is alternated between reference and sample compartment at a rate of 60 Hz. (or other fixed frequency). These two beams alternatively strike a single detector where their optical energy is converted to an electrical signal. The output of the detector is an alternating signal whose amplitude is proportional to the difference in intensities in the two channels. The reference signal is maintained constant by an automatic slit serve system achieve a 100% transmittance base line.

In Scanning Electron Microscope (SEM), an electron beam from a tungsten filament is focused by magnetic lenses on an area of surface 50-150 μm in diameter in a high vacuum chamber. The electron beam is composed of primary electrons and this beam can simply be reflected from the surface (the top layer of atoms) without any energy interchange, since the energy of primary electrons is high, much higher than the energy with which electrons are bound to nuclei, dissipation of this energy in the sample will knock electrons out of the atoms. These are secondary electrons, and their energies (lower than those of primary electrons) can vary because in most cases, the primary electrons may induce a number of ionization processes.

RESULT AND DISCUSSION

Fig. 2 shows the XRD pattern of TiO_2 thin films annealed at 300°C for 2 hour and it is confirmed that the material was not crystallized and it was in amorphous state. Fig. 3 shows the XRD pattern of the TiO_2 thin film annealed at 400°C for 2 h and the peaks observed at $2\theta = 25.3^\circ$ and 37.1° with

the plane (101) and (103) corresponds to the Anatase phase TiO_2 . The obtained values are closely coexisting with the JCPDS File No.89-4921. Hence the presence of TiO_2 was confirmed. The calculated grain size is 14 nm and it was calculated using the following scherrer formula.

$$D = \frac{0.9 \times \lambda}{\beta \cos \theta} \quad (1)$$

Where,

D = Grain size

λ = Wavelength of the X-ray source

β = Full Width Half Maximum

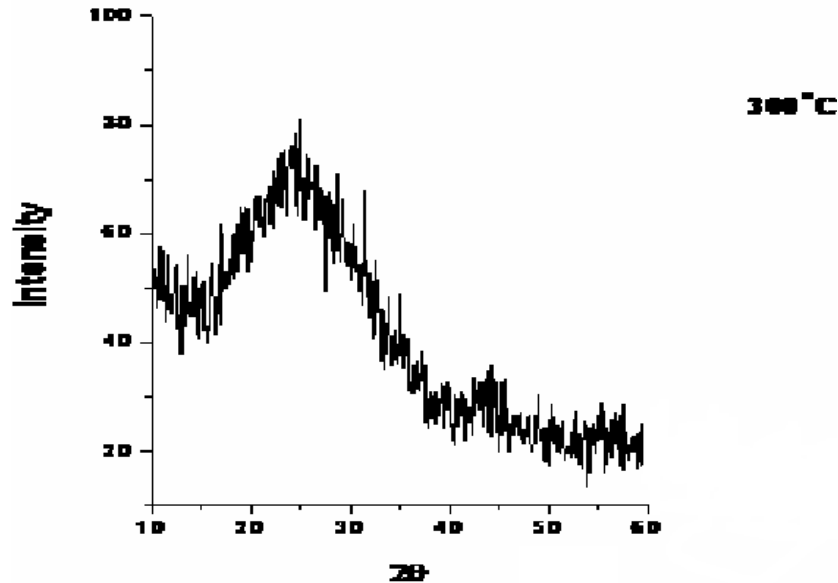


Fig 2 XRD Spectra of TiO_2 thin film at 300°C

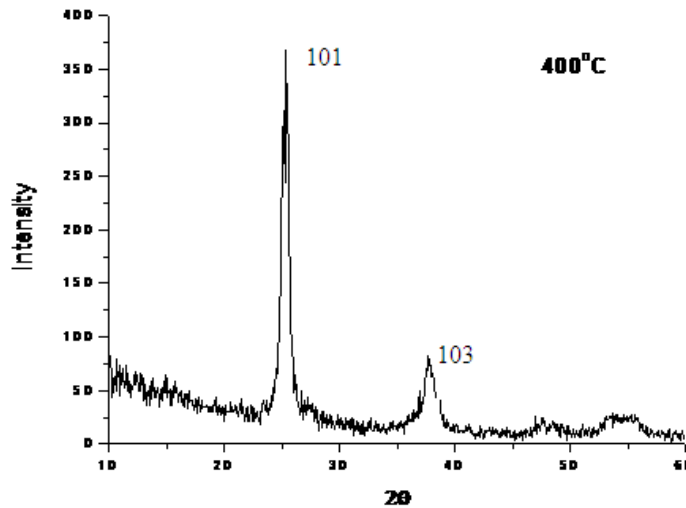


Fig 3 XRD Spectra of TiO_2 thin film annealed at 400°C

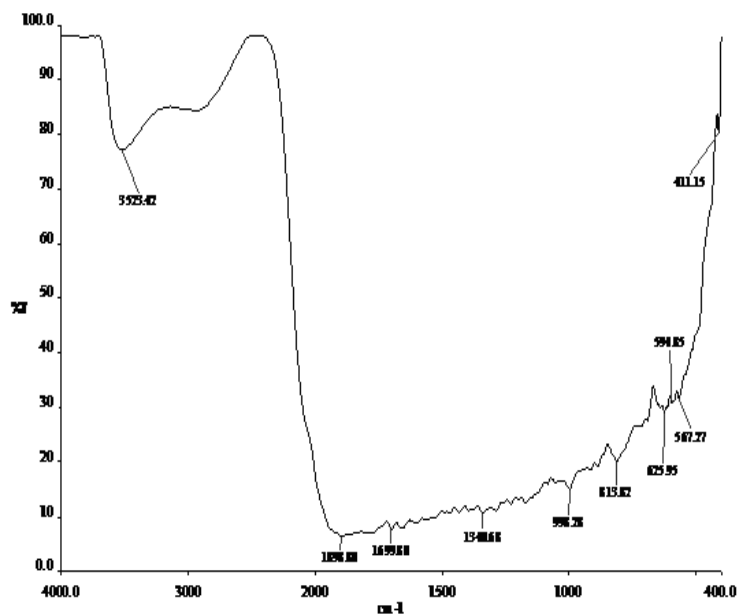


Fig 4. FTIR spectrum of TiO_2 thin film at 300°C

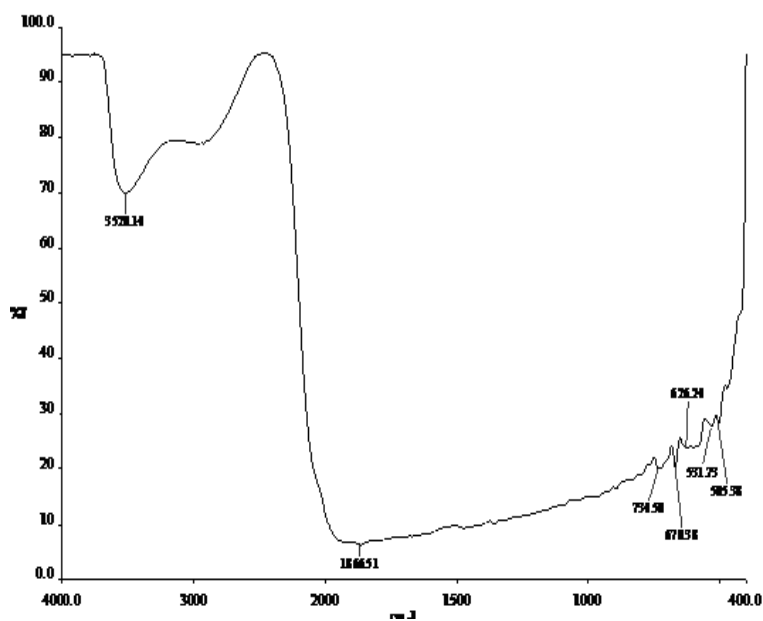


Fig. 5 FTIR spectrum of TiO_2 thin film annealed at 400°C

Fig 4. and 5 shows the FTIR spectrum of TiO_2 thin film annealed at 300°C and 400°C respectively. The peaks observed at 411.15 cm^{-1} , 560.20 cm^{-1} attributed to the presence of Ti-O bond and they were matched with the previous literature. The Peak around 3523.42 cm^{-1} observed due to the OH bond. It may be due to ethanol.

Fig. 6 and Fig. 7 are the UV vis NIR spectrum of the spin coated TiO_2 thin film annealed at 400°C for 2 hour. The film shows the maximum transparency of 85%. Fig 8 is the graph of $h\nu$ Vs $(\alpha h\nu)^2$. The point of X – axis in which the tangent of the curve intersects is known as the band gap of the TiO_2 thin film and it was to be 3.24 eV and

the value is closely coexisting with the literature values.

The theoretical and experimental investigation on the optical behavior of thin films deal with the optical reflection, transmission and absorption properties. From these properties it is easy to obtain optical constant. Thus optical studies lead to a variety of optical phenomena which have thrown considerable light on electronic structure of solids. Absorption studies provide an easy method for evaluation of optical energy band gap, absorption edge, optical transitions which may direct or indirect, allowed or forbidden and also nature of solid material.

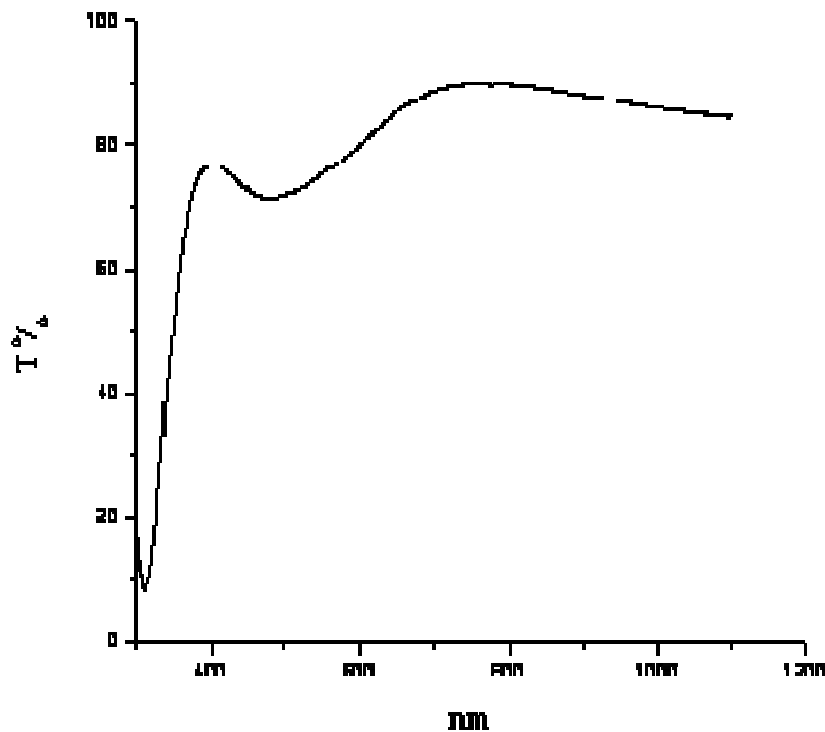


Fig. 6 UV Spectrum of TiO_2 thin film

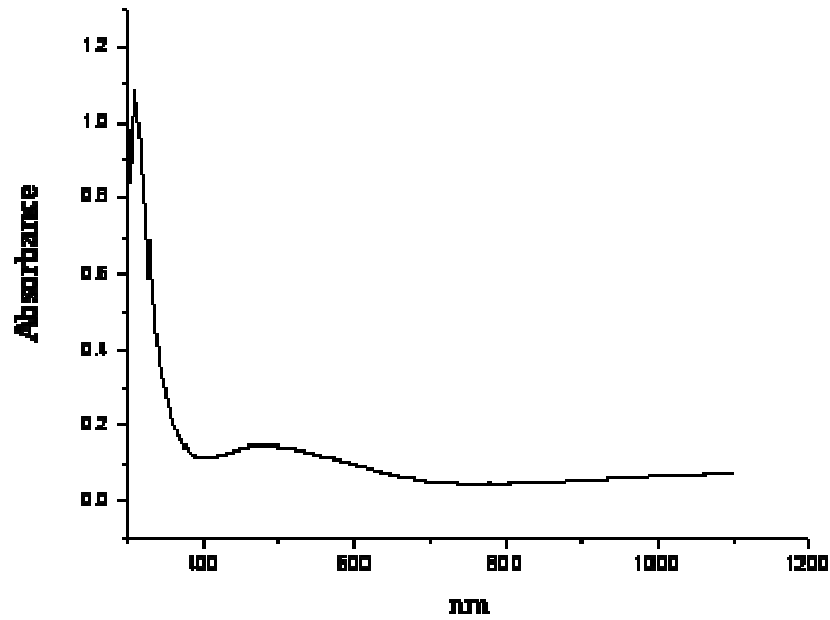


Fig. 7 Absorbance spectra of TiO₂ thin film

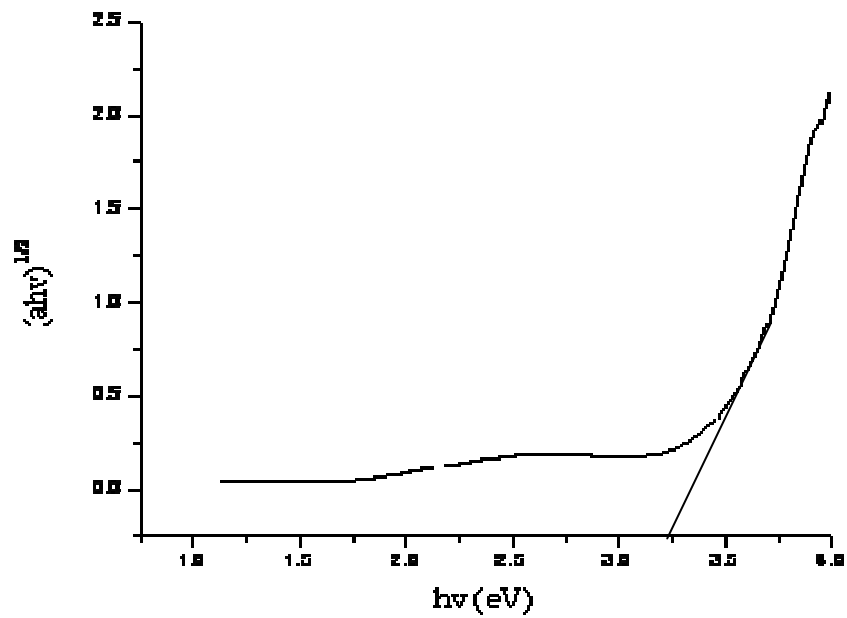


Fig. 8 Band gap of TiO₂ thin film

Fig 9(a-d) shows the different magnification views of Scanning Electron Microscopy of TiO₂ thin film annealed at 400°C for 2 hour. The pictures show island like morphology and the non homogeneity of the film. It may be improved by increasing the annealing temperature.

The SEM technique uses the intensity of the secondary electrons. Some of these electrons recombine with ions at the surface, as a result, photons are released. These electrons are basis for the SEM imaging capability and the contrast in the image is a result of difference in scattering from different surface areas, as result of geometry differences SEM has been widely used for visualization of organic surfaces. The main advantages of SEM are due to (i) much larger magnification are possible since electron wavelength is much smaller than photon wavelength and

(ii) the depth of field is much larger.

$$\begin{aligned} \text{The electron wavelength } \lambda_e &= h/mv_e \\ &= 12.2/\sqrt{v} \text{ \AA} \quad (2) \end{aligned}$$

The wavelength is 0.12Å for v=10,000 volt which is significantly less than 4000 Å to 7000 Å wavelength range of visible light. Hence the resolution of SEM can be much high than that of an optical microscope.

Advantages:

- (i) Large depth focus.
- (ii) High resolution.
- (iii) Crystal perfection.

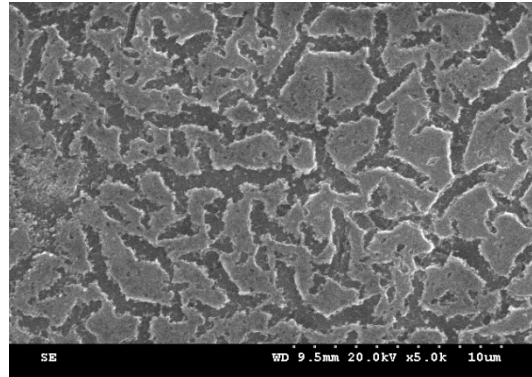


Fig.9 (a)

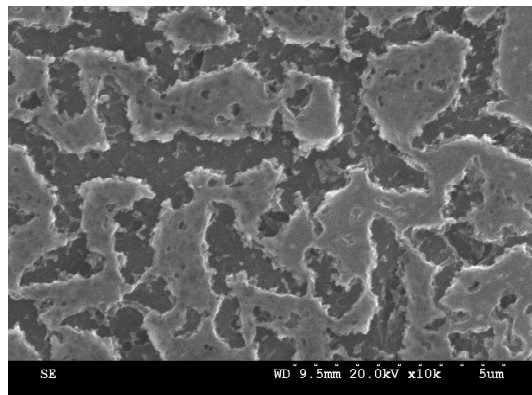


Fig.9 (b)

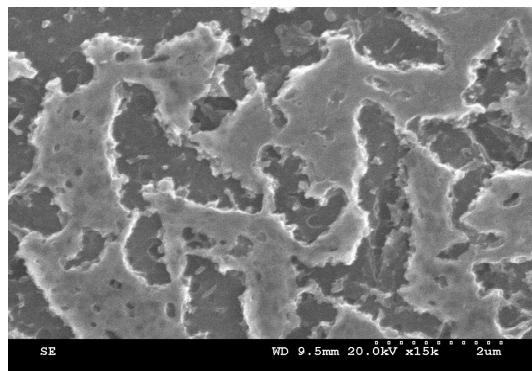


Fig.9 (c)

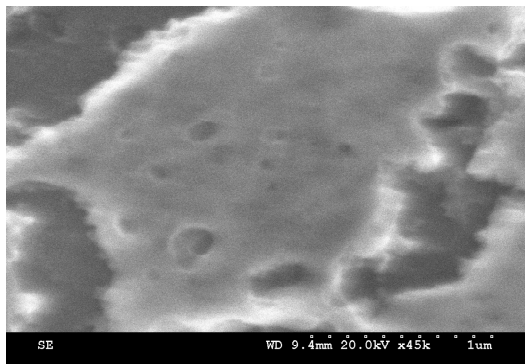


Fig. 9 (d)

Fig. 9 (a-d) SEM picture of TiO₂ thin film annealed at 400°C

CONCLUSION

The overview of different methods of thin film has been discussed briefly and the Sol-Gel technique is elaborated with advantages.

Preparation and characterization of TiO₂ thin film prepared by spin coating method and its properties were analyzed with respect to temperature variation. The crystallization of TiO₂ Anatase phase was confirmed by X-Ray diffraction studies. The crystallization of TiO₂ thin films tends to begin at 400°C annealing temperature.

The functional groups of the deposited films were analyzed using FT-IR

spectrum. The M-O-M band was assigned to the presence of Anatase TiO₂ phase. The optical properties of the film were studied with UV-VIS-NIR spectrophotometer. The deposited TiO₂ film annealed at 500°C shows high transparency about 85%. The band gap is found to be 3.24eV which coexisted with the literature value. The morphology of the thin film was analyzed with Scanning Electron Microscopy (SEM). The SEM pictures show island like morphology and the non homogeneity of the film. It may be improved by increasing the annealing temperature.

REFERENCES

1. Hui Huang , xi yao, *Journal of crystal growth* 268, 564-567 (2004).
2. P.S. Patil, S.H. Mujawar, A.I. Iramdar, S.B. Satale, *Appl. Surf.Sci.* 250, 117-123 (2005).
3. Ibrahim A., AL. Homardi, J.S. Thakur, R. Naik, G.W.Auner, G.Newaz, *Appl. Surf. Sci.* 253, 8607-8617 (2007).
4. P.S. Patil, S.H. Mujawar, A.I. Inamdar, P.S. Shinde, H.P. Deshmukh, S.B. Sadale *app. Surface Science* 252, 1643-1450 (2005).
5. Akira Nakajima, Nobuaki Hayashi, Yayoi Taniguchi, Yoshikazu Kameshima, Kiyoshikada. *Surface & Coatings Technology* 192, 112-116 (2005).